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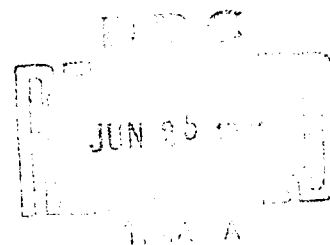
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# THE THEORY OF ACID DISSOCIATION IN SOLUTION

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U.S. ARMY BIOLOGICAL LABORATORIES  
FORT DETRICK, FREDERICK, MARYLAND

Translation by Sp/6 Charles T. Osterlag Jr.,  
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THE THEORY OF ACID DISSOCIATION IN SOLUTION

by N. A. Izmaylov

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U.S. ARMY BIOLOGICAL LABORATORIES  
FORT DETRICK, FREDERICK, MARYLAND

The Theory of Acid Dissociation in Solution. N. A. Izmaylov, (Journal of Physical Chemistry. Vol. XXVIII, Issue 11, 1954, pp. 2047-2066).

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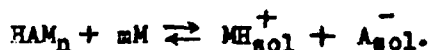
On the basis of a new theory of acid dissociation, an equation has been worked out which characterizes the dependency of acid strength on the physical and chemical properties of the solvents. The derived equation makes it possible, on the basis of independent data, to evaluate quantitatively the influence of solvents on the strength of acids and to estimate the magnitude of the differentiated action of solvents on acid strength.

#### Equilibrium Constants and Acid Strength in Solution

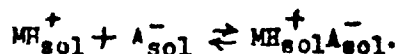
As was shown by us in a number of works [1], acid dissociation into ions in solution depends on a number of conjugated equilibria. It can be imagined that initially there takes place a reaction between the acid and the solvent with the formation of addition compounds of different composition and different polarity [2-4]



The compound  $HAM_n$ , as a result of subsequent solvation, dissociates with the formation of solvated ions:

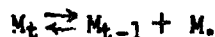
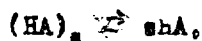


The ions formed in solvents with a low dielectric constant interact between themselves with the formation of ion pairs [4, 5] :



The relationship between concentrations (activities) of products of these reactions  $HA$ ,  $HAM_n$ ,  $MH_{sol}^+$ ,  $A_{sol}^-$ ,  $MH_{sol}^+ A_{sol}^-$  depends on the properties of  $HA$  and  $M$ ; that is, on the properties of the acid and the solvent, and also on their concentrations.

In many cases, the process of acid association is accompanied by a change in the ratio of acid and solvent, i.e., accompanied by the reactions:



However, the effect of these equilibria on the acid strength is appreciable only in concentrated solutions. In dilute solutions, in which the thermodynamic constants are known, the next to last reaction (ion pairing) goes on up to infinite dilution, but the last reaction (dimerization or association) practically doesn't get started. For example, in very concentrated aqueous

solutions the molecules of nitric acid are associated; with the addition of water the associates are replaced by the products of the interaction of nitric acid and water with the composition  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  [4] and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  [3]; simultaneously the degree of association of water changes. During subsequent dilution these products dissociate into solvated ions. If during this process the dielectric constant of the solution is not great, then this takes the place of a solvent such as dioxane in the mixture, and the ions of nitric acid form "ion molecules" or ion pairs.

The equilibrium constants in the above diluted reactions may be expressed as follows: the constant of the first reaction - instability constant

$$K_{\text{instab}}^* = \frac{a_{\text{HA}}^*}{a_{\text{HAM}_n}^*} \quad (1)$$

The index \* over  $a$  shows that the activities are relative to the infinitely dilute solution of HA in the solvent M; the value  $a_M^*$  - the number of solvent moles - is introduced into the constant as a constant value in the diluted solution. For the second equilibrium constant, also considering the constancy of the value  $a_M^*$ , we will express the following equation:

$$K_{\text{dis}} = \frac{a_{\text{MH}^+}^* a_{\text{A}^-}^*}{a_{\text{HAM}_n}^*}, \quad (2)$$

and finally, for the third equilibrium constant we will put down

$$K_{\text{ass}}^{-1} = \frac{a_{\text{MH}^+}^* a_{\text{A}^-}^*}{a_{\text{MH}^+}^* | \text{A}^-}_{\text{sol}}}. \quad (3)$$

The acid dissociation constant is determined by the usual methods from data on electrical conductivity or from data on cell potentials with and without transference ( $K_{\text{obs}}$ ), that is, with the help of methods which evaluate directly the activity of the ions and determine the activity of the remaining substances (which do not take part in the transfer of ions and do not determine the potentials of the electrodes) based on difference; it presents the relationship:

$$K_{\text{obs}} = \frac{a_{\text{MH}^+}^* a_{\text{A}^-}^*}{a_{\text{nondissociated substance}}^*},$$

in which the value  $a^*$  of the nondissociated substance is determined by the sum of the activities of the free acid molecules, the activity of the products of combination, and the activity of the ion pairs, that is

$$a_{\text{nondissociated, sub}}^* = a_{\text{HA}}^* + a_{\text{HAM}_n}^* + a_{\text{MH}_{\text{sol}}^+ \text{A}_{\text{sol}}^-}^*$$

Such an addition is based on the fact that in the diluted solutions to which the thermodynamic constants refer,  $a^* = C$  and  $\gamma^* = 1$ . Then

$$K_{\text{ob}} = \frac{a_{\text{MH}_{\text{sol}}^+}^* a_{\text{A}_{\text{sol}}^-}^*}{a_{\text{HA}}^* + a_{\text{MH}_{\text{sol}}^+ \text{A}_{\text{sol}}^-}^* + a_{\text{HAM}_n}^*} \quad (4)$$

Having expressed in equation (4) the activities  $a_{\text{HA}}^*$ ,  $a_{\text{HAM}_n}^*$  and  $a_{\text{MH}_{\text{sol}}^+ \text{A}_{\text{sol}}^-}^*$  over the activity of the solvated ions with the help of equations (1), (2), and (3), we get

$$K_{\text{obs}} = \frac{a_{\text{MH}_{\text{sol}}^+}^* a_{\text{A}_{\text{sol}}^-}^*}{\frac{a_{\text{MH}_{\text{sol}}^+}^* a_{\text{A}_{\text{sol}}^-}^*}{K_{\text{diss}} K_{\text{instab}}^{-1}} + \frac{a_{\text{MH}_{\text{sol}}^+}^* a_{\text{A}_{\text{sol}}^-}^*}{K_{\text{diss}}} + \frac{a_{\text{MH}_{\text{sol}}^+}^* a_{\text{A}_{\text{sol}}^-}^*}{K_{\text{ass}}^{-1}}} =$$

$$= \frac{1}{\frac{1}{K_{\text{diss}} \cdot K_{\text{instab}}^{-1}} + \frac{1}{K_{\text{diss}}} + \frac{1}{K_{\text{ass}}^{-1}}} = \frac{1}{\frac{K_{\text{instab}}^* + 1}{K_{\text{diss}}} + \frac{1}{K_{\text{ass}}^{-1}}}$$

For convenience we will write the resulting equation in the form:

$$K_{\text{obs}}^{-1} = (K_{\text{instab}}^* + 1) K_{\text{diss}}^{-1} + K_{\text{ass}} \quad (5)$$

From the equation it follows that the inverse value of the common dissociation constant (association constant) is the sum of the invariant values characterizing the conversion of ions in the nondissociated molecules HA and  $\text{HAM}_n$  and in the ion pairs  $\text{MH}_{\text{sol}}^+ \text{A}_{\text{sol}}^-$ ; consequently it is an invariant value.

In a number of particular cases, the equation (5) is simplified and used in that form.

In solvents with a high dielectric constant (more than 20) there is a lack of ion association and  $K_{\text{obs}}^{-1} = K_{\text{diss}}^{-1} (K_{\text{instab}}^* + 1)$ ; in media with a very low dielectric constant  $K_{\text{obs}}^{-1} = K_{\text{ass}}$ , since  $K_{\text{diss}}^{-1} (K_{\text{instab}}^* + 1) \ll K_{\text{ass}}$



It is usually erroneously assumed that acids become strong, when  $K_{obs}^{-1} = 1$  ( $\rho K = -1, K = 0$ ). In reality, acids just like any other electrolytes, become strong when  $K_{diss}^{-1} = 0$ , and  $K_{obs} = \infty$ , that is, when in the solution there is a lack of molecules ( $K_{diss}^{-1} = 0$ ), and ion associates ( $K_{ass} = 0$ ).

#### Derivation of the Basic Equation for the Dependency of Acid Strength on the Properties of the Solvents

We will look at the influence of solvents with a comparatively high dielectric constant, in which there is no association of ions ( $K_{ass} = 0$ ). In this case

$$K'_{obs} = \frac{K_{diss}}{K_{instab}^* + 1} \quad (6)$$

We will examine first the influence of the solvent on the value of the dissociation constant

$$K_{diss} = \frac{a_{MH_{sol}}^* + a_{A_{sol}}^*}{a_{HAM_n}^*}$$

For this we will put down the reaction constant  $HA \rightleftharpoons H^+ + A^-$ , taking place in a medium with an infinitely high dielectric constant and chemically not reacting with the substance  $HA$ . The reaction constant, expressed in activity units (see below), and relative to this standard medium

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}}, \quad (7)$$

has the significance of the intrinsic acidity constant of the substance and characterizes the ability of the substance  $HA$  to liberate its proton regardless of the medium.

The relationship between this constant  $K_a$  and the dissociation constant  $K_{diss}$  is established by exchanging the unit activity  $a$  with the product of the activities  $a^*$ , relative to the infinitely diluted solution in the given medium  $M$  as well as to the standard medium in the activity coefficients  $\gamma_0^\infty$ , that is the product of  $a^* \gamma_0^\infty$ . then

$$K_a = \frac{a_{MH_{sol}}^* a_{A_{sol}}^*}{a_{HAM_n}^*} \cdot \frac{\gamma_0^\infty MH_{sol} \gamma_0^\infty A_{sol}^-}{\gamma_0^\infty HAM}, \quad (8)$$

In equation (8) there is no other relationship of the activity  $a^*$  than  $K_{diss}$ . Consequently,

$$K_{diss} = \frac{\gamma_{OHAM_n}^{\infty}}{\gamma_{OH_{sol}}^{\infty} \gamma_{A_{sol}^-}^{\infty}} \quad (9)$$

The common neutral activity coefficients  $\gamma_o^{\infty}$ , in contrast to the usual concentration activity coefficients  $\gamma^*$ , characterize the energy changes of ions not in connection with a change in their concentration but in connection with a change of the solvent. They are coefficients of transition from the usual activities  $a^*$ , relative to the infinitely dilute solution, as well as to the standard, and to the activities  $a$ , which are relative to a common standard condition, that is  $a = a^* \gamma_o^{\infty}$ . The superscript  $\infty$  denotes a selected standard medium (the dielectric constant equals  $\infty$ ); the subscript  $o$  shows that the activity coefficients  $\gamma_o^{\infty}$  are proportional to the concentration activities  $a^*$ . From this, it follows that all the constants considered here are thermodynamic constants.

In order to solve equation (9), we analyze the significance of the value of  $\ln \gamma_o^{\infty}$  for the ions and molecules.

The activity coefficients  $\gamma_o^{\infty}$ , just as any other activity coefficients, are determined by the process of transferring the substances (molecules or ions) from the standard medium with an infinitely high dielectric constant into the given medium, that is

$$kT \ln \gamma_o^{\infty} = kT \ln \frac{a_i}{a_i^*} = A_i,$$

and consequently  $\ln \gamma_o^{\infty} = \frac{A_i}{kT}$  (the process  $A_i$  relates to one molecule or to one ion).

According to Born [6], the change of the potential energy of the ion, when it is transferred into the medium  $M$  with a dielectric constant  $D$ , is expressed thus:

$$A_n = \frac{e^2 Z^2}{2Dr},$$

However, our subsequent research showed [6-8] that the activity coefficients  $\gamma_o^{\infty}$  are determined, not only by the energy change of the ions in connection with the change of the dielectric constant  $D$ , but also with the energy change of ions in connection with the solvation of the ions with the dipole molecules of the solvents, that is, also, of the value  $A_{sol}$  which depends on the dipole moment and the structure of the molecules in the solvent. In this manner, the energy change of an anion when it is transferred from a standard medium to the given medium  $M$  is determined by the sum of  $A_n + A_{sol}$  and

$$\ln \gamma_o^{\infty} = \frac{A_n + A_{sol}}{kT} = \frac{e^2 Z^2}{2 D k T r_{A_{sol}}} + \frac{A_{sol} A_{sol}^-}{kT} \quad (10)$$

In determining the activity coefficient  $\gamma_D^\infty$  of the proton (ion  $MH_{sol}^+$ ), it is necessary to consider that a chemical reaction takes place between the proton and the molecules of the solvent with the formation of an  $MH^+$  ion according to the reaction  $M + H^+ \rightleftharpoons MH^+$ . The  $MH^+$  ion, in its turn, is solvated by the solvent; therefore the energy change of the proton when it is transferred from the medium with the infinitely great dielectric constant  $D$  to the given medium is determined not only by the sum of the process  $A_n + A_{sol}$ , but also by the chemical process  $A_x$  of adding the proton to the molecules  $M$ , that is -

$$\ln \gamma_D^\infty = \frac{A_x + A_n + A_{sol}}{kT}.$$

The sum of the operations  $A_n + A_{sol}$  is expressed just the same for the anion  $A_{sol}^-$ , that is

$$A_n + A_{sol} = \frac{e^2 Z^2}{2Dr_{MH^+}} + A_{sol}(MH^+).$$

The energy of the chemical reaction will be determined by the maximum work involved in the reaction  $H^+ + M \rightleftharpoons MH^+$

$$A_x = kT \ln K_{a(M)} - kT \sum \ln a_i,$$

in which  $K_{a(M)} = \frac{a_{H^+} a_M}{a_{MH^+}}$  represents the acidity constant of the lyonium ions

of the solvent and characterizes the stability with which the proton lyonium ion  $MH^+$  is held in the standard medium. As the activity coefficients are related to the operation of transforming the proton into a lyonium ion, at their numerically equal concentrations (activities) ( $H^+$  and  $MH^+$ ) the equation for  $A_x$  takes the form:

$$A_x = kT \ln K_{a(M)} - kT \ln a_M,$$

and the value  $\ln \gamma_{DMH_{sol}^+}^\infty$  is determined by the expression

$$\ln \gamma_{DMH_{sol}^+}^\infty = \ln K_{a(M)} - \ln a_M + \frac{e^2}{2DkTr_{MH_{sol}^+}} + \frac{A_{sol}(MH_{sol}^+)}{kT}. \quad (11)$$

The activity coefficients of the uncharged addition compound  $HAM_n$  may be expressed by  $\gamma_D^\infty = \frac{a_{HA}}{a_{HAM_n}^*}$  and determined by the operation of converting the substance  $HA$  into the substance  $HAM_n$  (just as previously under the conditions of a numerical equality of the concentrations  $HA$  and  $HAM_n$ )

$$A = kT \ln K_{instab} - kT \ln a_M^* = kT \ln K_{instab}^*,$$

in as much as

$$K_{instab}^* = \frac{K_{instab}}{a_M^*}, \text{ i.e. } \ln \gamma_{CHAM_n}^\infty = \ln K_{instab}^* \quad (12)$$

The sense of the activity coefficient  $\gamma_{CHAM_n}^\infty$  may also be described in the following manner. Assume that  $\gamma_{HA_{sol}}^\infty$  and  $\gamma_{MH_{sol}}^\infty$  are equal units, then equation (9) will take the form

$$K_{diss} = K_a \gamma_{CHAM_n}^\infty$$

and consequently,  $\gamma_{CHAM_n}^\infty$  represents the coefficient, which shows how the capacity of the substance  $HAM_n$  for isolating the solvated proton is changed in comparison with the capacity of substance  $HA$  to isolate the proton, that is, it shows the change in the intrinsic acidity of substance  $HA$  under the influence of solvation, thus

$$\gamma_{CHAM_n}^\infty = \Delta K_a \text{ and } \ln \gamma_{CHAM_n}^\infty = \ln \Delta K_a \quad (13)$$

By making a logarithmic equation (9) and substituting the value  $\gamma_{O.i}^\infty$  in it, we get

$$\ln K_{diss} = \ln K_a + \ln \Delta K_a - \ln K_{a(m)} + \ln a_M^* - \frac{e^2}{2DkT\epsilon_{MH_{sol}^+}} - \frac{A_{sol}MH^+}{kT} - \frac{e^2}{2D_MkT\epsilon_{A_{sol}^-}} - \frac{A_{sol}A^-}{kT} \quad (14)$$

or

$$\ln K_{diss} = \ln K_a + \ln \Delta K_a - \ln K_{a(m)} + \ln a_M^* - \sum \frac{e^2}{2D_MkT\epsilon_i} - \frac{\sum A_{sol}}{kT}, \quad (15)$$

and the common dissociation constant  $K_{obs}$  without a calculation of ion association is written

$$\ln K'_{obs} = \ln K_a - \ln \Delta K_a + \ln a_M^* - \ln K_{a(m)} - \ln (K_{instab}^* + 1) - \sum \frac{e^2}{2D_MkT\epsilon_i} - \frac{\sum A_{sol}}{kT}; \quad (16)$$

finally, by potentiating and substituting the result obtained in equation (5)  $K_{obs}^{-1} = (K'_{obs})^{-1} + K_{ass}$ , we get

$$K_{obs}^{-1} = \frac{K_a(m)(K_{instab}^* + 1)}{K_a \Delta K_a a_M^*} \exp \left\{ \sum \frac{e^2}{2D_m k T r_i} + \frac{\sum A_{sol}}{kT} \right\} + K_{ass} \quad (17)$$

By placing in equation (17) the expression for  $K_{ass}$  in agreement with Bjerrum's Theory, we finally get

$$K_{obs}^{-1} = \frac{K_a(m)(K_{instab}^* + 1)}{K_a \Delta K_a a_M^*} \exp \left\{ \sum \frac{e^2}{2D_m k T r_i} + \frac{\sum A_{sol}}{kT} \right\} + \left( \frac{4\pi N}{1000} \right) \left( \frac{e^2}{D_m k T} \right)^3 Q_y(l), \quad (18)$$

where  $Q_y(l) = \int_2^l e^{-y} y^{-4} dy$ , and in which  $y = \frac{e^2}{D k T r}$ ,  $l = \frac{e^2}{D k T a}$ .  
and with this,  $r$  = the distance between ions, and  $a$  = the sum of the ions' radii.

#### The Dependency of the Dissociation Constant on the Properties of the Solvent and the Acid

It is difficult to compare the equation that was brought out with experimental data, in as much as it is impossible to determine experimentally the value of the activity coefficients  $\gamma_{\pm}^{\infty}$ , relative to a medium with an infinitely great dielectric constant and the value of the natural acidity constant  $K_a$ . We can only make qualitative conclusions on how the properties of the solvents have an influence on the value of individual members in the equations (16) and (17) on the strength of the acids.

#### Influence of the Dielectric Constant of the Solvent

The influence of the dielectric constant of the solvent is related both in connection with the change in ion association and in connection with a change in ion energy.

In media with a high dielectric constant, the value for the thermodynamic constant is  $K_{ass}^{-1} = 0$ , in as much as association is negligible [9]. In any case this takes place in aqueous solutions (the dielectric constant equals 80).

Strictly speaking, at infinite dilution (to which state the thermodynamic constants refer) the association doesn't appear in any solvent. However, as numerous research [10] and our calculations [11] show, association originates in

solvents with a low dielectric constant even when very strongly diluted, which must be looked at as saturated dilutions.

A solvent with a high basicity and a high dielectric constant (for example, hydrazine) will change any, even weak, acids into strong electrolytes. The changing of acids into true electrolytes also takes place in basic solvents with a low dielectric constant (for example, in pyridine). This is evidenced by the formation of salts with these bases (for example, with ammonia, pyridine, and aniline) and acids, and their complete ionization in media with a high dielectric constant (for example, in water). However, in media with a low dielectric constant, in contrast to media with a high dielectric constant,  $K_{ass}^{-1}$  is not equal to zero, and this causes a weakening of acid strength and the deviation of the classical dissociation constant ( $K_{obs}^{-1}$ ) from zero. The value of the constant in these solutions will be determined only by a constant opposite to the ion association constant.

In as much as all acids in a given solvent have a common cation - a lyonium ion - the difference in the ion association of the acids depends on the difference in the radii of their anions. In media with a low dielectric constant, this leads to a differentiation of acid strengths.

These reasons cause a differentiation of salt strengths so considerable that in differentiated solvents - in acetone and others - we succeeded in performing a separate titration of a mixture of two bromides or iodides by precipitation.

In order of magnitude, the values of the acid association constants should be equal to the salt association constants. However, usually the acid constants (in other words the lyonium salts) are noticeably lower than salts with inorganic cations or salts of quaternary ammonia bases, but closer to the constants of mono-, di-, and tri-substituted bases with free hydrogen capable of forming a hydrogen bond. Thus, in pyridine (dielectric constant equals 12.5) the pK value of tetraethylammonium picrate is 2.9, of diethylammonium picrate-3.57, and of pyridine picrate (a solution of picric acid in pyridine)-3.65, that is of the same order as diethylammonium picrate. This reduction of the pK takes place at the expense of the formation of a hydrogen bond between the ions. The pK values of other strong acids in the same solvent are not great [1, 11] and are strongly differentiated:

hydrogen fluoride .....	pK = 8.3
hydrogen chloride .....	pK = 5.4
hydrogen bromide .....	pK = 4.0
hydrogen iodide .....	pK = 3.23
perchloric acid .....	pK = 3.12
tetraethylammonium iodide .....	pK = 3.28
tetraethylammonium chlorate .....	pK = 3.16

No less sharp is the difference between the dissociation constants of substances (including acids) capable of hydrogen bonding and those that cannot form them in aniline (D=7.2).

The reduction of the dielectric constant explains not only the formation of ion associations but also the increase of ion energies  $\frac{e^2 Z^2}{2 D k T r_i}$ . This

leads to an increase in the value of the exponential term in equation (17), that is, to an increase in  $K_{obs}^{-1}$  and consequently to a weakening of acid strength. This weakening occurs in solvents with dielectric constants ( $D$  is greater than 20) where association still doesn't occur. In reality, during the transfer from water to ethanol, in which the association of ions of strong electrolytes in dilute solutions is still lacking, there is observed a considerable weakening of acid strengths [12] and a considerable increase in the activity coefficients  $\gamma_i$  [6].

#### The Effect of Molecules in the Solvents on the Solvation of Acid Ions

The influence of the dielectric constant on the properties of ions cannot be examined separately from the effect of solvation. The ion energy depends on both values, which are introduced into the exponential member of the equation  $\exp\left\{\sum \frac{e^2}{2 D k T r_i} + \frac{\sum A_{scl}}{kT}\right\}$ . The energy of solvation  $A_{scl}$  has a negative sign in

relation to the energy of the ions. Therefore, the energy of the ions grows just as much with a decrease in the dielectric constant as with a decrease of the energy of solvation, that is, the less the value of  $\sum A_{scl}$ , the greater the energy of the ions. Consequently the value of the exponent  $\sum \frac{e^2}{2 D k T r_i} + \frac{\sum A_{scl}}{kT}$

more or less determines the significance of the value of  $\sum A_{scl}$ . On the other hand, this value drops with an increase in solvation and dielectric constant. In the event of a large numerical value for  $\sum A_{scl}$  and a high dielectric constant, the exponent rapidly approaches zero, and the entire exponential term approaches unity.

Probably a high energy value of ion solvation by solvents containing hydroxyl groups is the reason that in alcohols the acid dissociation constants are usually greater than in solvents with the very same basicity and dielectric constant but not containing hydroxyl groups [7, 12].

#### Control of the Natural Basicity of a Solvent and the Natural Acidity of an acid $K_{a(M)}$ and $K_a$

Unfortunately, neither one nor the other value can be readily observed in as much as it is impossible to measure them in media in which a protolytic equilibrium is realized.

From the preceding section it follows that the values for the natural acidity of the acid and the solvent should determine the status of the protolytic equilibrium, especially in media with a high dielectric constant and a high capability for solvation in as much as in this case, the exponential term in the equation (17) strives for unity and ion association is absent. In these media

$$K_{obs}^{-1} = \frac{K_{a(M)} (K_{instab}^* + 1)}{K_a \Delta K_{a \cdot M}^*}$$

From the equation, it follows that the constant  $K_{inst}$  will increase in connection with an increase in the natural acidity constant of the acid (that is, its capability to lose a proton), and with a decrease in the acidity of the solvent or an increase of its basicity (that is, its capability to add a proton). At the present time we can not evaluate the significance of these constants by experimental means but it is possible to successfully compute them theoretically. Experimental evaluation is possible only relative to the constants for the natural acidity (basicity) of the solvents. We will examine this method in the section devoted to the evaluation of the change in acid strength during the transfer from solvent to solvent.

#### The Effect of the Interaction of Nondissociated Acid Molecules with the Solvent ( $K_{inst}^* + 1$ ) and $\Delta K_a$

The interaction of acids with a solvent has been established by numerous methods of physico-chemical analysis and by optical methods. Our cryoscopic investigations showed [2] that carboxylic acids with alcohols (methanol, ethanol, butanol) form compounds with a composition of 1:2, and with differentiated solvents (acetone [2], acetonitrile, nitrobenzene [13]) 1:1; phenols with alcohols and with differentiated solvents form compounds with a composition of 1:1.

Investigation of the absorption spectrum and the fluorescence spectrum [14], and also the Raman spectra [15], of the products of combining acids with solvents in benzene and in pure solvents showed their identity; this indicates the conclusions about composition, made on the basis of investigating benzene solutions, being justified also for pure solvents.

The instability constants  $K_{inst}^*$  of the products from the combination of acids with acetone [2], acetonitrile, and nitrobenzene [13], measured in benzene, have approximately the value of  $0.5 \times 10^{-3}$  for carboxylic acids and  $0.5 \times 10^{-2}$  for phenols. The instability constants for the products of the interaction of carboxylic acids with alcohols in benzene have the values  $5 \times 10^{-5}$ , and for the phenols with alcohols,  $1 \times 10^{-1}$ .

From the instability constants, it follows that  $(K_{inst}^* + 1) \approx 1$  and  $\log(K_{inst}^* + 1) \approx 0$ . In pure nonaqueous solvents with a dielectric constant equal to 20, the constants are probably greater than in benzene with a dielectric constant equal to 2, which can lead to a considerable value for the term  $\ln(K_{inst}^* + 1)$ .

However, the formation of combination products during the equivalent relations of the acid and the solvent during the physico-chemical analysis of similar systems indicates completely the conversion of acid into a solvated form in dilute solutions. Our optical investigations [14, 15] also confirm this. Thus, in the Raman spectra of carboxylic acids [15] in alcohols (containing as little as 10 mole percent), there is displayed only one frequency of the  $C=O$  group, approximately the same in all alcohols and homologous to the frequency of the group in the combination product of the composition  $HAM_2$ .

Thus, in all probability, there takes place in dilute aqueous and alcoholic solutions a complete transition of the  $HA$  molecules into a solvated form. In this case,  $K_{inst}^* \ll 1$ , and  $\ln(K_{inst}^* + 1)$  returns to zero.





It is interesting to note that the value  $a_M$  in equation (17) arises only in connection with the expression of concentration in molalities ( $a_M$  - the number of gram molecules of solution in 1000 grams) with the expression of concentration in mole fractions  $a_M = 1$ .

From everything said, it follows that during a decrease of the dielectric constant of the solvent, its basicity, and its capability for solvating ions and molecules, the strength of the acids drops; on the contrary, with an increase of the dielectric constant and an increase in the basicity and capability for solvation, the strength of the acids increases. Within a limit,

$$\text{when } K_{ass}^{-1} = 0, \exp \left\{ \sum \frac{e^2}{2.3 DK T r_i} + \frac{\sum A_{sol}}{kT} \right\} \rightarrow 1, K_{instab}^* \ll 1,$$

the strength of the acids depends on  $K_a$  and  $K_{a(M)}$ . If during this  $K_{a(M)} \ll K_a$ ,  $K_{obs}^{-1}$  tends to zero, and the acid becomes a strong acid.

#### Changes in Acid Strength Under the Influence of Solvents

It is possible to conduct a quantitative evaluation of the correctness of the expounded equation (17) by a comparison of acid strength in different solvents, that is, by observing the change of acid strength during the transfer from one solvent, taken as the standard one (usually water is selected as such a solvent), to any nonaqueous solvent. Then the change in acid strength can be compared with independent data, that is, with single activity coefficients  $\gamma_D$ , compared to an aqueous solution in its capacity as a standard state.

For accomplishing such a comparison, we will express the value of acid strengths in pK values. For simplicity we will examine dissociation in solvents with a relatively high dielectric constant, in which there is an absence of ion association, that is, we will examine the value  $K'_{obs}$ . Accepting that  $pK' = \log K'_{obs}$ , from equation (16) we get

$$pK'_{obs(M)} = -\log K_a + \log K_{a(M)} - \log \Delta K_a - \log a_M^* + \log (K'_{instab} + 1) + \sum \frac{e^2}{2 \cdot 2.3 DK T r_i} + \frac{\sum A_{sol}}{2.3 \cdot kT}. \quad (19)$$

The difference of the pK values in two solvents, for example in the solvent M and in water ( $H_2O$ ), is expressed

$$pK'_M - pK'_{H_2O} = \log \frac{K_{a(M)}}{K_{a(H_2O)}} + \log \frac{a_{H_2O}^*}{a_M^*} + \sum \frac{e^2}{4.6 k T r_i} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \sum A_{sol}}{2.3 kT} + \log \frac{(K'_{instab} + 1)_M}{(K'_{instab} + 1)_{H_2O}} - \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}}. \quad (19)$$

From equations (10) and (11) it follows that in this equation, the sum of the first four members represent the difference of the average activity coefficients

$\gamma_D^\infty$  of the ions  $A_{sol}^-$  and  $MH_{sol}^+$  in a nonaqueous solvent and in water. This difference represents none other than the sum of the logarithms of the activity coefficients  $\gamma_r$  of the acid ions in the given solvent (M) while approaching infinite dilution, relative to the infinitely diluted aqueous solution as well as to the standard

$$\begin{aligned} & \log \frac{K_{a(M)}}{K_{a(H_2O)}} + \log \frac{a_{H_2O}^*}{a_M} + \sum \frac{c^2}{4.6 kT} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \Sigma A_{sol}}{2.3 kT} = \\ & = (\log \gamma_{0MH_{sol}}^+ + \log \gamma_{0A_{sol}}^-)_M - (\log \gamma_{0H_3O_{sol}}^+ + \log \gamma_{0A_{sol}}^-)_{H_2O} = \\ & = \log \gamma_{0MH_{sol}}^+ + \log \gamma_{0A_{sol}}^- = 2 \log \gamma_D \end{aligned} \quad (20)$$

Upon introduction of the average activity coefficients  $\gamma_D$  of the acid ions, the first four members in equation (20) represent none other than

$$2 \log \gamma_{D, ion} \cdot$$

The expression  $\log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} - \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}}$ ,

taken with an opposite sign, in its turn, represents the difference of the activity coefficients ( $\gamma_D^\infty$ ) of the nondissociated molecules HA in the solvent M

and in water, that is, it represents the activity coefficients of the acid HA in the medium M, relative to the infinitely dilute solution compared to the standard, that is,

$$\begin{aligned} & \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}} - \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} = \\ & = \log \gamma_{0mol(M)}^\infty - \log \gamma_{0mol(H_2O)}^\infty = \log \gamma_{0mol} \end{aligned} \quad (21)$$

Generally the expression (19) can be shortened

$$\Delta_p K = 2 \log \gamma_{D, ion} - \log \gamma_{0mol} \quad (22)$$

The equation (22) can also be derived directly from an examination of the acid transfer from one solvent (for example, water) to another (nonaqueous) solvent with the help of common activity coefficients  $\gamma_c$ , related to the infinitely dilute aqueous solution, compared to the standard.

In reality, the effect of the solvents on a common dissociation constant can be expressed by the equation

$$K'_{obs}(H_2O) = K'_{obs}(M) \frac{\gamma_c MH^+_{sol} \gamma_c A^-_{sol}}{\gamma_c Mcl}, \quad (23)$$

from where

$$pK'_m - pK'_{H_2O} = 2 \log \gamma_{0ion} - \log \gamma_{0mcl}. \quad (24)$$

It is interesting to note that the equation (19), in its turn, can be derived from equation (23), in as much as the terms for the ions are derived independently from the investigation of the effect of the solvent on the activity of the acid ions, and  $\log \gamma_{c mol}$  is from the investigation of the

effect of the solvent on the activity of a nondissociated substance.

In reality, from the preceding works [6-8], we, as a result of theoretical considerations, established that  $\log \gamma_0$  of the ions is determined by the expression

$$\log \gamma_{0ion} = \frac{1}{2} \log K_r + \frac{1}{2} \log \frac{a_{H_2O}^*}{a_M^*} + \frac{1}{2} \sum \frac{e^2}{4\pi\epsilon kT} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \Sigma A_{sol}}{2.3 kT},$$

in which  $K_r = \frac{a_{H_3O^+}^* + a_M^*}{a_{MH^+}^* + a_{H_2O}^*}$  represents the constant of proton exchange

between the lyonium ion and the hydronium ion  $MH^+ + H_2O \rightleftharpoons H_3O^+ + M$ .

measured in the medium  $M$ . We factored the  $\log \gamma_{0ion}$  term into the

terms  $\log \gamma_0^{base} = \frac{1}{2} \log K_r + \frac{1}{2} \log \frac{a_{H_2O}^*}{a_M^*}$ , dependent only on the proton exchange reaction, and into the term  $\log \gamma_0^{el} = \frac{1}{2} \sum \frac{e^2}{4\pi\epsilon kT} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right)$ ,

dependent on the electrostatic interaction of the ions with the solvent. Under the very same conditions we worked out methods for the experimental determination of the values  $\log \gamma_0$  and their separation into  $\log \gamma_0^{base}$  and  $\log \gamma_0^{el}$ .

We also showed [7] that  $\log \gamma_{0mol}$  is determined by the expression:

$$\log \gamma_{0mol} = \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}} - \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} = \log \frac{K_{instab}^*(M)}{K_{instab}^*(H_2O)} - \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} \quad (25)$$

and established methods of determining them.

The equation (22) can also be derived directly from an examination of the acid transfer from one solvent (for example, water) to another (nonaqueous) solvent with the help of common activity coefficients  $\gamma_c$ , related to the infinitely dilute aqueous solution, compared to the standard.

In reality, the effect of the solvents on a common dissociation constant can be expressed by the equation

$$K'_{obs}(H_2O) = K'_{obs}(M) \frac{\gamma_c MH^+_{sol} \gamma_c A^-_{sol}}{\gamma_c Mcl}, \quad (23)$$

from where

$$pK'_m - pK'_{H_2O} = 2 \log \gamma_{oion} - \log \gamma_{omcl}. \quad (24)$$

It is interesting to note that the equation (19), in its turn, can be derived from equation (23), in as much as the terms for the ions are derived independently from the investigation of the effect of the solvent on the activity of the acid ions, and  $\log \gamma_{c mol}$  is from the investigation of the

effect of the solvent on the activity of a nondissociated substance.

In reality, from the preceding works [6-8], we, as a result of theoretical considerations, established that  $\log \gamma_o$  of the ions is determined by the expression

$$\log \gamma_{oion} = \frac{1}{2} \log K_r + \frac{1}{2} \log \frac{a_{H_2O}^*}{a_M^*} + \frac{1}{2} \left[ \frac{e^2}{4.6 kT} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \Sigma A_{sol}}{2.3 kT} \right],$$

in which  $K_r = \frac{a_{H_3O^+}^* a_M^*}{a_{MH^+}^* a_{H_2O}^*}$  represents the constant of proton exchange

between the lyonium ion and the hydronium ion  $MH^+ + H_2O \rightleftharpoons H_3O^+ + M$ ,

measured in the medium  $M$ . We factored the  $\log \gamma_{oion}$  term into the

terms  $\log \gamma_o^{base} = \frac{1}{2} \log K_r + \frac{1}{2} \log \frac{a_{H_2O}^*}{a_M^*}$ , dependent only on the proton exchange reaction, and into the term  $\log \gamma_o^{el} = \frac{1}{2} \left[ \frac{e^2}{4.6 kT} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) \right]$ ,

dependent on the electrostatic interaction of the ions with the solvent. Under the very same conditions we worked out methods for the experimental determination of the values  $\log \gamma_o$  and their separation into  $\log \gamma_o^{base}$  and  $\log \gamma_o^{el}$ .

We also showed [7] that  $\log \gamma_{omcl}$  is determined by the expression:

$$\log \gamma_{omcl} = \log \frac{\Delta K_a(M)}{\Delta K_a(H_2O)} - \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} = \log \frac{K_{instab}^*(M)}{K_{instab}^*(H_2O)} - \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} \quad (25)$$

and established methods of determining them.

By substituting the  $\log \gamma_{\text{ion}}$  and  $\log \gamma_{\text{mol}}$  values in equation (24), we get the equation (26)

$$pK'_M - pK'_{H_2O} = \Delta pK = \log K_r + \log \frac{a_{H_2O}^*}{a_M^*} + \sum_i \frac{c^2}{4.6 kT r_i} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \Sigma A_{sol}}{2.3 kT} + \log \frac{(K_{instab.}^* + 1)_M}{(K_{instab.}^* + 1)_{H_2O}} - \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}} \quad (26)$$

which is identical to equation (19), in that  $K_r = K_{a(M)} / K_{a(H_2O)}$ .

In reality by substituting the expression for

$$K_{a(M)} = \frac{a_{H^+} a_M}{a_{MH^+}} \text{ and } K_{H_2O} = \frac{a_{H^+} a_{H_2O}}{a_{H_3O^+}},$$

we receive

$$K_r = \frac{K_{a(M)}}{K_{a(H_2O)}} = \frac{a_M a_{H_2O}}{a_{H_2O} a_{MH^+}}.$$

The experimentally measured value  $K_r$  is distinguished from this value in that it is not determined in a medium with an infinitely large dielectric constant, but in medium  $M$ . During the quantitative evaluation of the change in acid strength under the influence of the solvents over  $\gamma_o$ , this doesn't play a substantial role, in that the small differences between the values are quantitatively compensated by the difference in other members ( $\gamma_o^*$  and  $a^*$ ), and that the sum of the terms  $\log \gamma_o^{base} + \log \gamma_o^*$  is determined independently.

The produced conclusion opens the possibility of the quantitative checking of equation (19) with the help of data about the  $\log \gamma_o$  values of ions and molecules. The term  $\log \gamma_o^{base}$  also enables the comparative acidity or basicity of the solvents to be evaluated.

#### Appraisal of the Change of Acid Strength from Independent Data (Comparison of $\Delta pK$ and $\log \gamma_o$ )

Appraisal of the influence of solvents on acid strength and on the relationship in their strength on the basis of the  $\log \gamma_o$  value of ions and  $\log \gamma_o$  of molecules which are arrived at independently will be done in subsequent works where we will also examine the change in acid strength from the  $\log \gamma_o^{base}$ ,  $\log \gamma_o^*$ ,  $\log K$ , and  $\Delta \Sigma A_{sol}$  values.

As an example in the present work, we will examine only the simplest case of such a computation from independent data where the effect of the solvent on the acid strength depends mainly on the energy change of the lyonium ion and the acid anion.

Such a case, most probably of all, will be appropriate for the appraisal of the change in one type of acid strength in a series of solvents, close in structure, and especially in water-enriched mixtures of a nonaqueous solvent with water. In these solvents the  $K_{instab.}^*$  values are much smaller and are close to each other. In connection with this, the  $\log \frac{(K_{instab.}^* + 1)_M}{(K_{instab.}^* + 1)_{H_2O}}$  value approaches zero.

The corresponding  $\log \frac{\Delta K_{a(H_2O)}}{\Delta K_{a(H_2O)}} = \log \frac{K_{a(H_2O)}}{K_{a(H_2O)}}$  values become constant but not great in effect. Then in equation (19) the only significant members will be the first four members, equal to the logarithm of the single activity coefficients, that is,

$$\Delta pK' = pK'_M - pK'_{H_2O} = 2 \log \gamma_{ion}$$

We will examine to what extent this simple relationship concurs with experimental data. On the basis of data about the emf of cells of strong acids without transference and on the basis of the density of strong acid vapors, we established the significance of the  $\log \gamma_c$  value and showed that  $\log \gamma_c$  for a number of strong acids in any given solvent practically concurred, depending, according to type, only on the properties of the solvent [6]. The result of this is that in the expression

$$2 \log \gamma_c = \log \gamma_{cMH_{sc}^+} \gamma_{cA_{sc}^-} = \log \gamma_{cMH_{sc}^+} + \log \gamma_{cA_{sc}^-}$$

$\log \gamma_{cMH_{sc}^+}$  is a constant term for any acid and the  $\log \gamma_{cA_{sc}^-}$  values for the various simple anions are close and considerably less than  $\log \gamma_{cMH_{sc}^+}$ .

Stemming from the electromotive force of the cells for hydrogen chloride without transference, we found that the value  $2 \log \gamma_{c,cl}$  has the following values in various solvents [6, 7]:

methanol .....	3.82	formic acid .....	8.0
ethanol.....	5.00	acetic acid.....	10.0
butanol.....	6.0	ammonia.....	32.0

As we already said, the  $2 \log \gamma_{c,ion}$  value depends slightly on the acid anion, therefore we will compare the  $2 \log \gamma_{c,ion}$  value for HCl in alcohol with the  $\Delta pK$  values of the substituted phenols [12].

Table 1.

Acids	Methanol		Solvents		Butanol	
	$\Delta pK$	$2 \log \gamma_c$	$\Delta pK$	$2 \log \gamma_c$	$\Delta pK$	$2 \log \gamma_c$
Nitrophenols	3.97*	3.82	5.44	5.00	5.49	5.2
Dinitrophenols	3.82	3.82	4.19	5.00	4.34	5.2
Averages	3.90	3.82	4.82	5.00	4.94	5.2

\* Average value

The comparison with the data for phenols in alcohols is done because the greatest accord with experimental data will be observed in solvents of the same type with regards to the acids, with which they react only as acceptors of protons. From the table it follows that the average  $\Delta pK$  value for nitrophenols is in good agreement with the  $2 \log \gamma_c$  value of hydrochloric acid, even though the individual  $\Delta pK$  values are different from the  $2 \log \gamma_c$  value by almost one pK unit.

Figure 1 also testifies to the fact that the  $\Delta pK$  value is determined to a considerable degree by the  $2 \log \gamma_{O_{ion}}$  value. Figure 1 depicts the relation

between the  $pK$  value of a number of carboxylic acids [17] and phenols [21] in aqueous ethanol to  $2 \log \gamma_{O_{ion}}$  of hydrogen chloride. From figure 1,

it follows that the relation  $\Delta pK = f(2 \log \gamma_{O_{ion}})$  in reality approximates a linear relation. Usually with solutions containing a small percentage of alcohol, this relation deviates somewhat from rectilinearity but subsequently becomes linear. The slope is close to  $45^\circ$ , as is to be expected from theory. For comparison on the graph, there is a dotted straight line drawn for  $2 \log \gamma_{O_{ion}}$ .

It is located in the middle. It is interesting to note that the points for p-nitrophenols fall on the straight line for  $2 \log \gamma_{O_{ion}}$ ; the points for m-nitrophenols are located lower, and the point for carboxylic acids is above the

straight line for  $2 \log \gamma_{O_{ion}}$ . The divergence between the location of the straight lines for the phenols and carboxylic acids in ethanol is on the order of two  $pK$  units; between the carboxylic acids, on the order of one  $pK$  unit. Such a characteristic relationship of the  $pK$  value to  $2 \log \gamma_{O_{ion}}$  in mixtures

of aqueous dioxane is depicted in figure 2. The divergence between the curved lines for carboxylic acids is also on the order of a  $pK$  unit.

Figure 3 depicts the relationship  $\Delta pK = f(2 \log \gamma_{O_{ion}})$  for phenols, and for aromatic and aliphatic carboxylic acids in alcohols (deferring the average  $\Delta pK$  values [12]). From this figure, it follows that: 1) the relation between the  $\Delta pK$  value and  $2 \log \gamma_{O_{ion}}$  is linear; 2) the  $\Delta pK$  value of the substituted phenols and  $2 \log \gamma_{O_{ion}}$  - are of the same order; 3) the position of the straight lines for aliphatic and aromatic carboxylic acids is different; 4) all the straight lines do not pass through the origin which shows the various



effects on the properties of the acid molecules, the alcohol and the water.

The previous calculations of the  $2 \log \gamma_{\text{ion}}$  value of hydrogen chloride in acetone and its mixtures with water, which were conducted by V.V. Aleksandrov, show that even for acetone, the  $2 \log \gamma_{\text{ion}}$  value of the acids determines to a considerable degree the change of acid strength. This follows from a comparison of the  $2 \log \gamma_{\text{ion}}$  value with the  $\Delta pK$  value.

From these facts it follows that, just the same as with alcohol,  $2 \log \gamma_{\text{ion}}$  HCl are very close to the  $\Delta pK$  values of nitrophenols, considerably less than the  $\Delta pK$  values of carboxylic acids, and considerably more than the  $\Delta pK$  values of dinitrophenols.

A comparison of the  $2 \log \gamma_{\text{ion}}$  values of strong acids with the  $\Delta pK$  for carboxylic acids in various solvents: in a number of alcohols, in aqueous methanol, ethanol, dioxane and acetone and in other solvents, shows that the deviation between them is greater than for phenols.

Table 2.

Solvent	$2 \log \gamma_{\text{base}}$	$2 \log \gamma_{\text{el}}$	$2 \log \gamma_{\text{c}}$	$\Delta pK^*$ carboxylic acid	$\Delta pK^*$ nitrophenols	$\Delta pK^*$ dinitrophenols
50% acetone	0.14	0.8	0.94	1.40	1.00	0.46
90% "	1.04	3.28	4.32	5.00	3.61	2.79
100% "	1.68	4.4	6.08	7.20	6.44	4.72

\* average values are cited.

The deviation of  $\Delta pK$  from the  $2 \log \gamma_{\text{ion}}$  value of strong acids may be the result of the difference of the  $2 \log \gamma_{\text{ion}}$  value of the acids investigated and a considerable  $\log \gamma_{\text{c}}$  value for nondissociated acid molecules. In order to solve this problem it is necessary to compare the  $\Delta pK$  and  $2 \log \gamma_{\text{ion}}$  values of the acids that were investigated by themselves. Determining the  $\log \gamma_{\text{ion}}$  values of weak acids becomes possible on the ground that the  $\log \gamma_{\text{c}}$  values of ions of infinitely dilute solutions show, similarly, the mobility of ions at infinite dilution, with additive values.

The additivity of  $\log \gamma_{\text{c}}$  allows us to find the  $\log \gamma_{\text{c}}$  of the ions of a weak acid HX based on the equation:

$$2 \log \gamma_{\text{OHX}} = 2 \log \gamma_{\text{OHCl}} + 2 \log \gamma_{\text{cHX}} - 2 \log \gamma_{\text{cHCl}}$$

We calculated the  $\Delta \log \gamma_{\text{ion}}$  values of a series of carboxylic acids in methanol and ethanol from the data stated above with reference to  $\log \gamma_{\text{Cl}}$  of hydrogen chloride and to  $\log \gamma_{\text{e}}$  of the silver salts of these carboxylic acids and  $\text{AgCl}$ . We found the  $\log \gamma_{\text{Cl}}$  and  $\Delta \log \gamma_{\text{AgX}}$  values from data on the solubility of these salts obtained by Kolthoff and Lingane [19] with the aim of evaluating the effect of solvents on the strength of acids. The calculation was carried out according to the formula [7, 8]:

$$\log \gamma_{\text{e}} = \log \frac{a_{\text{H}_2\text{O}}^*}{a_{\text{M}}^*} = \log \frac{m_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}^*}{m_{\text{M}} \gamma_{\text{M}}^*},$$

applied as in the case of the difficultly soluble salts  $\gamma_{\text{M}}^*$  and  $\gamma_{\text{H}_2\text{O}}^* \approx 1$ .

The resulting values of  $\Delta \log \gamma_{\text{e}}$  for carboxylic acids in table 3 are compared with the corresponding  $\Delta \text{pK}$ . From the table, it follows that the difference between them comprises 2-3 logarithmic units. This means that the change of acid strength depends on the change of energy of the ions as well as the molecules.

Table 3.

Acid	Methanol			Ethanol		
	$\Delta \log \gamma_{\text{e ion}}$ acid	$\Delta \text{pK}$	$\Delta \text{pK} - \Delta \log \gamma_{\text{e ion}}$	$\Delta \log \gamma_{\text{e ion}}$ acid	$\Delta \text{pK}$	$\Delta \text{pK} - \Delta \log \gamma_{\text{e ion}}$
Benzoic	3.22	5.2	1.98	4.04	5.93	1.89
O-Nitrobenzoic	3.42	5.43	2.01	4.40	6.28	1.88
M-Nitrobenzoic	2.66	4.81	2.15	3.54	5.81	2.27
P-Nitrobenzoic	2.62	4.96	2.34	3.40	5.45	2.05
Salicylic	2.56	4.92	2.36	3.08	5.62	2.56
Picric	1.04	4.00	2.96	1.04	3.13	2.09

The  $\Delta \log \gamma_{\text{e}}$  values determine the change of acid strength both in basic and acidic solvents. In accordance with the large negative  $\Delta \log \gamma_{\text{e ion}}$  value  $\approx -11.0$  in ammonia, all, even the weakest acids (hydrogen sulfide), and even neutral substances (urea) become equally strong acids with  $\text{pK} \approx 2-3$  [20]. Such a  $\text{pK}$  value is explained by the fact that in ammonia with a dielectric constant equal to 20, a noticeable association of ions takes place. In accordance with the great positive value of  $\Delta \log \gamma_{\text{e ion}}$  in acidic solvents rich in water, the acids become

weak. Thus,  $\Delta \log \gamma_{\text{e ion}}$  in acetic acid equals 10. In accordance with this, the  $\text{pK}$  of trichloroacetic acid in acetic acid becomes equal to 11, 64 [21]. The increase comprises 11  $\text{pK}$  units.

In this manner equations (19) and (22) obtained theoretically allow us to

estimate quantitatively the change of acid strength during the transition from one solvent to another with the help of single activity coefficients  $\gamma_0$  of the ions and molecules, which in turn may be obtained from independent data.

#### Comparison With Bronsted's Quantitative Theory

As it is known, Bronsted's quantitative theory [22] about the influence of the solvents on acid strength for uncharged acids leads to the expression:

$$\ln K_{HAM} = \ln K_a - \ln K_{a(M)} - \sum \frac{e^2}{2 D_M k T r} \quad (27)$$

A comparison of our equation (16) with Bronsted's equation (27) shows that the latter appears as a peculiar case of this equation. His equation is incomplete moreover in that it doesn't take into account the effect of ion association. The equation (16) brought out by us differs from Bronsted's equation by the values

$\ln(K_{instab}^* + L)$ ,  $\frac{\sum A_{scl}}{kT}$ , and  $\ln \Delta K_a$ . The difference in the member  $\ln a_M$  arises in connection with the fact that Bronsted's  $K_{HAM}$  is different from the constant  $K'_{obs}$  for the activity (concentration) of the solvent  $K'_{obs} = K_{HAM} a_M$ .

The incompleteness of Bronsted's equation appears not only as a result of the incompleteness of the arrangement applied by Bronsted for  $HAM \rightleftharpoons MH^+ + A^-$ , but also as a result of the incompleteness of the significance of the activity coefficients for the ions which Bronsted used, and also by the fact that he didn't calculate the activity change of the nondissociated acid molecules under the influence of the solvent.

From his equation, Bronsted made the conclusion that the logarithms for the constants of acids of the same charge type should be linear inversely relative to the value of the dielectric constant.

In reality it follows from (27) that the relative constant  $K_{rel}$  is expressed by the equation

$$pK_{rel} = -\log K_{rel} = \log \frac{K_{HAM}}{K_{HAM_0}} = \log \frac{K_{ex}}{A_{a_0}} + \sum \frac{e^2}{2.3 D k T} \left( \frac{1}{r_c} - \frac{1}{r_x} \right) = \text{const} + A \left( \frac{1}{D} \right), \quad (28)$$

in as much as the ratio of the  $K_a$  constants is fixed.

As we showed, experimental data do not always confirm this relationship [16]. It can also be shown that this equation is a peculiar case of a more general expression:

$$\begin{aligned}
pK_{rel} = \log \frac{K'_{a,c}}{K'_{a,x}} = \log \frac{K_{a,c}}{K_{a,x}} + \sum_i \frac{e^2}{4.3 \cdot DKT} \left( \frac{1}{r_c} - \frac{1}{r_x} \right) + \frac{A_{scl} A_{x^-} - A_{scl} A_c^-}{2.3 \cdot KT} + \\
+ \log \frac{\Delta K_{a,c}}{\Delta K_{a,x}} = \log \frac{(K_{instab}^* + 1)_c}{(K_{instab}^* + 1)_x} ,
\end{aligned} \tag{29}$$

which evolves from equation (16). This equation differs from equation (28) in the last three terms, whereupon the term  $\frac{A_{scl} A_{x^-} - A_{scl} A_c^-}{2.3 \cdot KT}$  shows

the different effect of the solvent dipoles on properties of the acid anions, and the last two terms - the effect of the solvent on the properties of the nondissociated acid molecules. The equation shows that in a general situation in accordance with the experiment, the pK<sub>r</sub> value does not appear as a linear function of 1/D.

Only in those cases, when the influence of the solvents on the nondissociated molecules is equal and the energy of ion solvation is the same (an absence of differentiating action), as this takes place with respect to acids of the same type and in a series of solvents of the same composition, then the last three terms become equal to zero and the pK value is linearly dependent on 1/D.

Similarly the comparison of equation (19) with the equation (arising on the basis of Bronsted's equation)

$$\begin{aligned}
pK'_M - pK'_{H_2O} = \log K_{a(M,c)} - \log K_{a(M)} + \sum_i \frac{e^2}{4.6 \cdot KT_r} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \\
+ \log \frac{a_{H_2O}^*}{a_M^*} = \log K_r + \sum_i \frac{e^2}{4.6 \cdot KT_r} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \log \frac{a_{H_2O}^*}{a_M^*} ,
\end{aligned} \tag{30}$$

shows, that in this equation as in Bronsted's basic equation, there is a complete disregard for the change in the activity of a nondissociated acid during its transfer from medium to medium, the solvation of ions, and the originating association of ions. In connection with this, the equation does not consider the differentiating action of the solvents on the acid strength and the limited applicability only during the examination of the effect of solvents of the same nature on acids of the same chemical group.

#### The Differentiating Action of a Solvent

In our previous works, it was established that there were four types of differentiating action of solvents on acid strength. The proposed treatment of the process of acid dissociation and the equation developed by us completely embrace these four types of differentiating action.

As we established, the first type is the differentiating action of acidic solvents on the strength of strong acids. From equation (17) it follows that such a differentiating action develops in solvents with a large value for  $K_{a(n)}$ , thanks to which the first term of the equation (17) becomes distinct from zero, even during the dissociation of substances with a large  $K_a$  value, that is, strong acids. During this, the strong acids display their own individual properties, dependent on the  $K_{a(n)}$  value.

However it must be emphasized that the differentiating action of strong acids is observed in practice only when their dielectric constants are not great. Thus acetic acid with a dielectric constant equal to 6 displays a differentiating action while formic acid with a dielectric constant equal to 57 does not. In just the same manner, (mono)chloroacetic acid with a dielectric constant equal to 20 does not display a differentiating action while trichloroacetic acid with a dielectric constant equal to 4.55 differentiates the strength of strong acids [23]. It is obvious that with acidic solvents, the differentiating action is connected with the emergence of ion association in solvents with a low dielectric constant.

The second type of differentiating action is the change in the relative strength of acids of various homologous groups [12, 16] under the influence of any solvents, particularly those not containing hydroxyl groups. When transferred to such differentiating solvents, the strength of acids of one homologous group changes approximately the same but distinct from the change in strength of acids from another homologous group. Such an action appears as a result of the fact that the  $\log \gamma_{\text{rel}}$  and  $\log \gamma_{\text{mol}}$  values are close for acids of

the same type and different for acids of a different type. This change of ion activity in acids of a different type is explained by the various solvation energies of ions,  $A_{s,i}$  and a different change of activity of the nondissociated molecules - with the  $(\log \Delta K_{a(n)} - \log \Delta K_{a(H_2C)})$  value which becomes rather

considerable during the transfer from a solvent of one type to a solvent of another type.

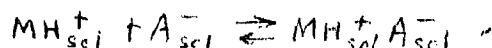
The third type is the differentiating action of basic solvents with a low dielectric constant. The value of this differentiating action is completely determined by the difference in ion association and ion pairs and numerically determined by the difference in the ion association constants ( $K_{aag}$ ).

The fourth type of differentiating action we call the changing of relative acid strength as a result of the interaction of the solvent with the substituents in the acid's radical. Such, as an example, is the influence of formalin on the strength of amino acids in connection with the interaction of the amino groups with formalin. From this examination of the effect of solvents, it follows that this differentiating action is similar to the differentiating action of the second type, and in this case it is a result of the changing of the characteristic acidity of a substance under the influence of the interaction of the substance with the solvent.

## Conclusions

1. Acid dissociation in solution takes place in several successive stages. In the first stage there is the formation of an addition product based on the reaction  $HA + n M \rightleftharpoons HAM_n$ , in the second stage, the formed addition product, as a result of subsequent solvation, dissociates with the formation of the solvated ions  $HAM_n + m M \rightleftharpoons MH_{sol}^+ + A_{sol}^-$ . In media with a low

dielectric constant there also takes place an association of ions into ion pairs



The usual dissociation constant appears as the function of the constants of all the specified constants  $K_{obs}^{-1} = (K_{instab}^* + 1) K_{diss}^{-1} + K_{ass}$ , in which  $K_{instab}^*$  is the equilibrium constant for the first process,  $K_{diss}$  for the second, and  $K_{ass}$  for the third.

2. The full equation brings out the dependency of acid strength on the properties of the solvent:

$$K_{obs}^{-1} = \frac{K_a(M) (K_{instab}^* + 1)}{K_a \Delta K_{a(M)}} \exp \left\{ \sum \frac{e^2}{2 D k T r_{ij}} + \frac{\sum A_{sol}}{kT} \right\} + K_{ass}$$

according to which the strength of the acid is determined by the natural acidity of the acid  $HA$ ,  $K_a$ , its change under the influence of the solvent  $\Delta K_a$  with an acidity constant (or basicity)  $K_{a(M)}$  of the solvent, a dielectric constant  $D$ , the energy of ion solvation  $A_{sol}$ , and the value of the Bjerrum ion association.

3. An equation was brought out, characterizing the change of acid strength under the influence of the solvents (in the absence of ion association)

$$\Delta pK' = pK'_{obs(M)} - pK'_{obs(H_2O)} = \log K_r + \sum \frac{e^2}{4.6 k T r_{ij}} \left( \frac{1}{D_M} - \frac{1}{D_{H_2O}} \right) + \frac{\Delta \sum A_{sol}}{2.3 k T} + \log \frac{a_{H_2O}^*}{a_M^*} + \log \frac{(K_{instab}^* + 1)_M}{(K_{instab}^* + 1)_{H_2O}} - \log \frac{\Delta K_{a(M)}}{\Delta K_{a(H_2O)}}$$

in which  $K_r$  is the constant of proton exchange between the molecules of a nonaqueous solvent and water,  $a_M^*$  is the molarity of the solvent in 1000g.

The developed expression can be described by the equation  $\Delta pK' = 2 \log r_{0,ion} - \log r_{0,rel}$ .

This equation makes it possible to determine the change of acid strength during the transfer from one solvent to another, from independent data.

4. On the basis of the additivity of single activity coefficients during an infinite dilution, a method is submitted for determining the activity coefficients  $\gamma_{\pm}$  of ions of weak acids, stemming from the activity coefficients  $\gamma_c$  of a strong acid and the salts of this strong acid and the corresponding weak acid with one and the same cation.

5. It is shown that Bronsted's equation characterizing the influence of the solvent on the strength of acids is a particular instance of the equation brought out by us.

6. On the basis of the equation that is developed, there are comments on four types of differentiating actions of solvents, which were established by us earlier. With the help of this equation one can estimate to what degree the differentiating action of the solvents depends on the interaction of the solvent with the nondissociated molecules and ions of the acid.

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21.IV 1954

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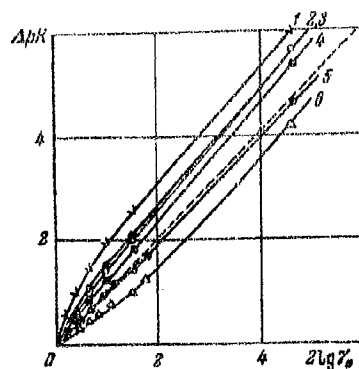


Figure 1. Relation of  $\Delta pK = pK_{\text{non-aqueous}} - pK_{H_2O}$  to  $2 \lg \gamma_{\pm}$  in aqueous ethanol: 1 - benzoic, 2 - chloroacetic, 3 - salicylic, 4 - formic acid; 5 - p - nitrophenol; 6 - 2,4 - dinitrophenol; dotted line ---  $2 \lg \gamma_{\pm}$

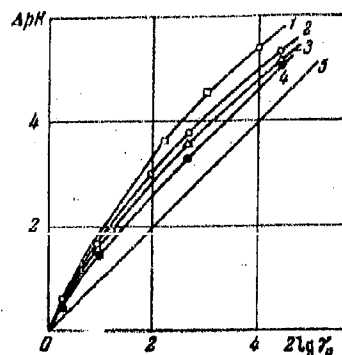


Figure 2. Relation of  $\Delta pK = pK_{\text{non-aqueous}} - pK'_{H_2O}$  to  $2 \lg \gamma_{\pm}$  in aqueous dioxane: 1 - benzoic, 2 - propionic, 3 - acetic, 4 - formic, 5 -  $2 \lg \gamma_{\pm}$  of hydrogen chloride.

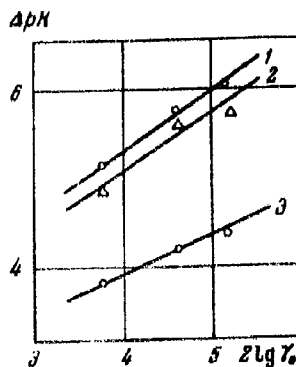


Figure 3. The relation of  $\Delta pK = pK_{\text{non-aqueous}} - pK_{H_2O}$  (average value) for methanol, ethanol and butanol as a function to  $2 \lg \gamma_{\pm}$ . 1 - aromatic carboxylic acids, 2 - aliphatic carboxylic acids, 3 - phenols.